

## C, H AND O ISOTOPE COMPOSITION OF VEGETABLE OILS FROM THE SOUTHERN AND NORTHERN HEMISPHERES

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Analysis of lipids in food control and environmental research is more important than ever in a time of increasingly complex globalization on food systems (food availability, supply, marketing, distribution, consumption, dietary patterns) implemented in ecosystems impacted by climate changes. In particular, is most important the control and characterization of the biosynthetic origin of plant (food) products and the study of how they evolve in changing environments. Production and consumption of vegetable oils (liquid) and fats (solid) were and are of key importance for human health and economic growth already since prehistoric time as evidenced by archaeological remains.

The potential of using compound-specific stable carbon isotope analysis ( $\delta^{13}\text{C}$ , in Ur relative to VPDB) of fatty acids by gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS) for authenticity control of nutritionally valuable and healthy vegetable oils and fats has been demonstrated previously (e.g., Spangenberg et al., 1998, and references therein). Hydrogen and oxygen isotope ratios ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ , in Ur relative to VSMOW) of plant organic compounds are mainly influenced by the isotopic composition of the primary water source (soil and ground waters) and their biosynthetic pathways. Thus, the variations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values in plant and their products through their relationship with humidity-precipitation and temperature conditions during plant growth may contribute to determining the purity of commercial vegetable oils and may provide information on their geographical origin (e.g., Richter et al, 2010, and references therein).

Maize, olive, sunflower, groundnut, soybean and rice oils differing in sites of growth in the southern and northern hemispheres were characterized by bulk oil stable isotopes ( $\delta^{13}\text{C}_{\text{bulk}}$ ,  $\delta^2\text{H}_{\text{bulk}}$ , and  $\delta^{18}\text{O}_{\text{bulk}}$ ) and fatty acids (FAs) concentrations and  $\delta^{13}\text{C}_{\text{FA}}$  values using elemental analysis/isotope ratio mass spectrometry, gas chromatography/mass spectrometry, gas chromatography/flame ionization detection and gas chromatography/combustion/isotope ratio mass spectrometry. Principal component analysis was applied to examine the inherent structure of the data.

The  $\delta^{13}\text{C}_{\text{bulk}}$  values of maize oils ( $-18.4$  to  $-14.9$  ‰) are typical for  $\text{C}_4$  plants; those of olive ( $-30.2$  to  $-28.2$  ‰), sunflower ( $-30.2$  to  $-29.2$  ‰), groundnut ( $-29.3$  ‰), soybean ( $-30.6$  ‰), and rice ( $-34.5$  ‰) oils are typical for  $\text{C}_3$  plants. The  $\delta^2\text{H}_{\text{bulk}}$  values vary from  $-161$  to  $-132$  ‰ for maize oils and  $-171$  to  $-109$  ‰ for  $\text{C}_3$  oils. The  $\delta^{18}\text{O}_{\text{bulk}}$  values of all oils vary between  $15.2$  and  $38.9$  ‰. The major  $\delta^{13}\text{C}_{\text{FA}}$  differences ( $>5$  ‰) within plant species render the inter- $\text{C}_3$ -species comparison difficult. These differences are explained in terms of variations in the lipid biosynthetic pathways and blend of vegetable oils of different FA composition and  $\delta^{13}\text{C}_{\text{FA}}$  values. The samples from the southern hemisphere are generally enriched in  $^{13}\text{C}$  compared to those from the northern hemisphere. This may be attributed to variations in  $^{13}\text{C}$  fractionation during  $\text{CO}_2$  fixation by different plant species and genotypes as well as different photosynthetic and physiological responses to changes in environmental conditions (temperature, atmospheric pressure, light intensities, water availability, nutrient supply). These  $\delta^{13}\text{C}$  differences may be enhanced by the different spatial and historical trends of atmospheric  $\delta^{13}\text{C}$  in the different geographical regions.

The greatest differences between the southern and northern hemispheres were observed in  $\delta^2\text{H}_{\text{bulk}}$  ( $p < 0.001$ ) for all  $\text{C}_3$  oils, and  $\delta^{13}\text{C}_{18:1}$  ( $p = 0.026$ ) for maize oils. Significant correlations were found between  $\delta^{13}\text{C}_{\text{bulk}}$  and  $\delta^{18}\text{O}_{\text{bulk}}$  ( $r = -0.35$ ,  $p < 0.05$ ) and  $\delta^2\text{H}_{\text{bulk}}$  and  $\delta^{18}\text{O}_{\text{bulk}}$  ( $r = 0.67$ ,  $p < 0.00001$ ). The slope of 3.4 of the  $\delta^2\text{H}_{\text{bulk}}-\delta^{18}\text{O}_{\text{bulk}}$  line determined for the  $\text{C}_3$  and  $\text{C}_4$  oils (excluding the outliers) can be compared to an evaporation slope, with higher  $\delta$ -values in warm regions and lower  $\delta$ -values in colder regions. Therefore, the good correlation of  $\delta^2\text{H}_{\text{bulk}}$  and  $\delta^{18}\text{O}_{\text{bulk}}$  and their connection to the

meteoric water line, and its inherent climatic-related factors (latitude, continentality, local temperature, and humidity), confirm the potential use of isotope composition of vegetable oils for characterization of their geographic origin and plant response to climatic changes. The proposed combined C, H and O (bulk and molecular) isotope analysis may also help to trace intercontinental variations of single seed/species C<sub>3</sub> and C<sub>4</sub> plant products, thus providing important information for archaeological, palaeoclimatic and palaeoecological studies.

## Reference

- Richter, E.K., Spangenberg, J.E., Kreuzer, M., Leiber, F., 2010. Characterization of rapeseed (*Brassica napus*) oils by bulk C, O, H, and fatty acid C stable isotope analyses. *Journal of Agricultural and Food Chemistry* 58, 8048–8055.
- Spangenberg, J.E., Macko, S.A., Hunziker, J., 1998. Characterization of olive oil by carbon isotope analysis of individual fatty acids: Implications for authentication. *Journal of Agricultural and Food Chemistry* 46, 4179–4184.